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## PREPARATION OF BORON TRIFLUORIDE FOR USE IN NEUTRON COUNTERS

By W. Hodges, M. I. Lloyd, and B. Weinstock

### INTRODUCTION

Boron trifluoride is used as the filling gas in ionization chambers and in proportional counters used for counting neutrons. The predominant reaction in these chambers is the  $(n-\alpha)$  reaction on  $B^{10}$  with thermal neutrons.

Since the performance of counters filled with  $BF_3$  is strongly dependent on the quality of the gas, an understanding of this dependence is helpful. While this subject is by no means completely understood, the following discussion summarizes some general information pertinent to this question.

One feature of a neutron counter which is generally desirable is a high counting efficiency, i.e., where a large percentage of the neutron flux gives rise to reaction. Since the number of neutrons captured is proportional to the concentration of  $B^{10}$  atoms in the chamber, by increasing the pressure of gas in the chamber, the efficiency can be increased. However, when the pressure is increased, higher voltages are necessary to collect the electrons. The use of higher voltages may then result in gas discharge in the counter, which will give rise to spurious counts. This is particularly true when small amounts of air and  $SiF_4$  are present as impurities. By the use of  $BF_3$  of increased  $B^{10}$  concentration (boron of over 80%  $B^{10}$  concentration is available), the necessity of using increased pressure to obtain higher efficiencies is somewhat alleviated. However the presence of impurities in the gas further manifest themselves by giving rise to poor operating characteristics. When pure  $BF_3$  is used in a counter, good voltage and bias plateaus are obtained. The pulses tend to be more uniform in size and well separated above the noise background. With impurities in the  $BF_3$ , this situation degenerates to the point where the counter cannot be reliably used.

The interior of the counter must be chemically clean before filling with  $BF_3$ . The presence of water in the interior is particularly objectionable. Water is known to form a hydrate with  $BF_3$  which hydrolyzes with the liberation of HF. HF can then react with any glass present in the counter to form  $SiF_4$  and more water. This chain process can then continue until the performance of the counter is no longer reliable.

The use of organic gaskets and wax seals in the construction of  $BF_3$  counters is generally objectionable. This is due to the fact that  $BF_3$  reacts readily with organic substances of this type. The reaction products from such processes will then interfere with the operation of the counter.

If an accurate knowledge of the  $B^{10}$  concentration in the chamber is desired, the isotopic concentration of the gas must also be accurately known. Aside from gas of enriched  $B^{10}$  concentration, where a direct measurement of the isotopic ratio is necessary, the use of the reported value of 18.4% as the percentage of  $B^{10}$  in normal boron is somewhat unreliable. This is due to the relatively large fractionation which can occur in processing boron compounds. Even commercial tanks of  $BF_3$  from the same company have shown differences in isotopic content of 1-2%. In addition to these possible corrections for the isotopic abundance, the molecular weight of  $BF_3$  vapor has been found to depend to a small extent on the temperature and pressure.\* This correction should also be made in precise calculations.

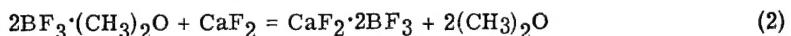
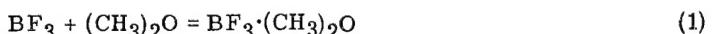
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\* Fisher and Wiedemann, Z. Allgem. Chem. 213, 106-114, (1933).

## METHOD OF PREPARATION

The method of preparation which will be described has yielded  $\text{BF}_3$  of the best known quality for use in neutron counters. It consists essentially of converting  $\text{BF}_3$  into calcium fluoborate and subsequently regenerating the  $\text{BF}_3$  by the thermal decomposition of this compound. The method was suggested by the fact that small samples of boron of enriched  $\text{B}^{10}$  concentration were available as the dimethyl ether compound for conversion into  $\text{BF}_3$ . This compound is readily converted to calcium fluoborate. The method has the additional advantages of giving high yields (over 85%) and requiring simple inexpensive apparatus.

The conversion from tank  $\text{BF}_3$  to purified  $\text{BF}_3$  will be described below. The process can be summarized by the three equations:



## Step 1

Boron Trifluoride, as obtained commercially, is about 90% pure, containing varying amounts of  $\text{SiF}_4$ , HF, and air. By the formation of  $\text{BF}_3 \cdot \text{Me}_2\text{O}$  these impurities are substantially removed except for small amounts dissolved in the ether compound. The apparatus which is used is shown in Figure 1.

The two gases are admitted simultaneously to the evacuated reaction bulb. The rates of flow of the gases can be judged roughly by means of the safety manometers and are regulated by means of the needle valves. The reaction bulb is cooled continuously with water because of the large amount of heat liberated by this reaction. When the system becomes "gagged" because of the accumulation of inert gas, it can be evacuated through the pump stopcock. The ether compound obtained is a colorless liquid and has a density given by the empirical relation  $d = 1.603 - 0.00124T$  ( $T$  = degrees absolute).\* The liquid obtained can be stored in a ground glass stoppered bottle (the joint should be greased to prevent its freezing). It will gradually darken with time due to decomposition, but this has not been found detrimental to its subsequent use.

## Step 2

The apparatus used for the conversion of  $\text{Me}_2\text{O} \cdot \text{BF}_3$  into calcium fluoborate is shown in Figure 2. About 2 moles of  $\text{CaF}_2$  are used per mole of ether compound. This represents a fourfold excess which is not entirely necessary. The  $\text{CaF}_2$  is pumped on at about  $300^\circ\text{C}$  for a few hours in order to dry it. The presence of water in  $\text{CaF}_2$  will lower the yield of  $\text{BF}_3$  eventually obtained by an amount proportional to the quantity of water present. But, since  $\text{CaF}_2$  usually contains only about 0.5%  $\text{H}_2\text{O}$ , thoroughly outgassing it is not considered an essential part of the procedure.

The ether compound reacts with the  $\text{CaF}_2$  at a rapid rate at  $100^\circ\text{C}$ . In bringing the furnace up to temperature, it is found that the liquid is first absorbed by the  $\text{CaF}_2$  at about  $80^\circ\text{C}$ , forming a slurry in the reaction flask. The reflux condenser is used to prevent serious loss of the ether compound, since the vapor pressure of the liquid is about 200 millimeters Hg at  $100^\circ\text{C}$ . The ether is collected in a graduated centrifuge tube kept at dry ice temperature. The yield as calculated from the amount of ether collected is about 93% when 10-20 cubic centimeter of liquid is used. The last traces of ether are pumped out of the reaction bulb before transferring it to the line for Step 3. The reaction bulb is kept at  $100^\circ\text{C}$  during this operation. The presence of any residual ether can be detected by putting dry ice on the U-tube. If the pressure in the system, as measured on the McLeod gauge, decreases when this is done, ether is still being liberated. Fluocarbon grease is used for the stopcocks on this line.

\* Report A-2120. "Separation of Isotopes", I. Kirshenbaum, N. Sabi, P. W. Schutz. The numerical values given in this discussion are all taken from this report.

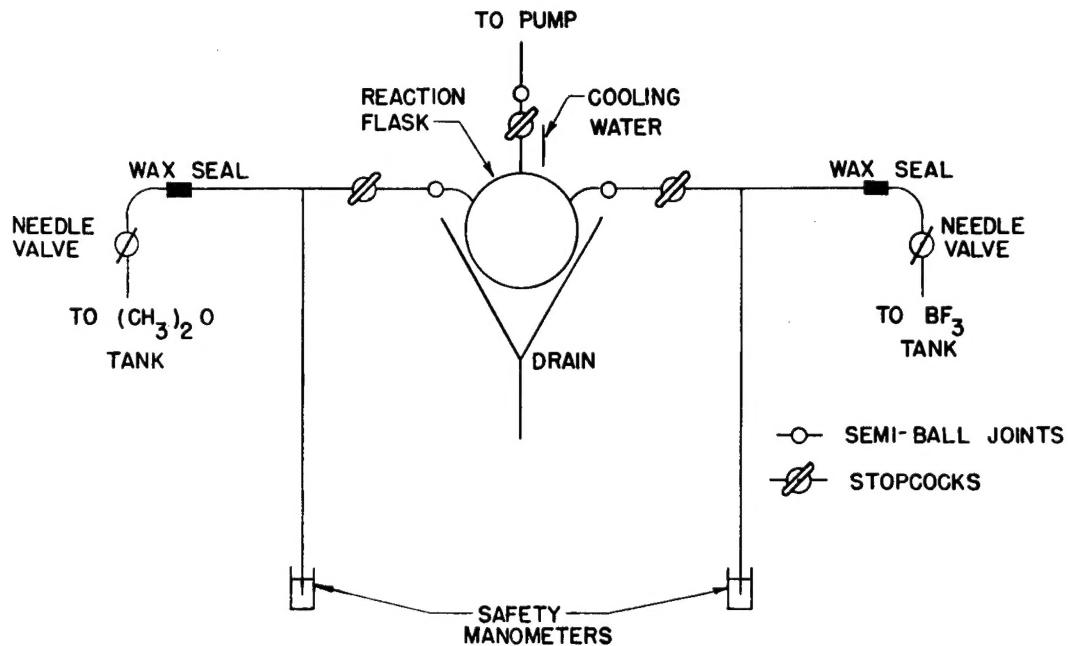
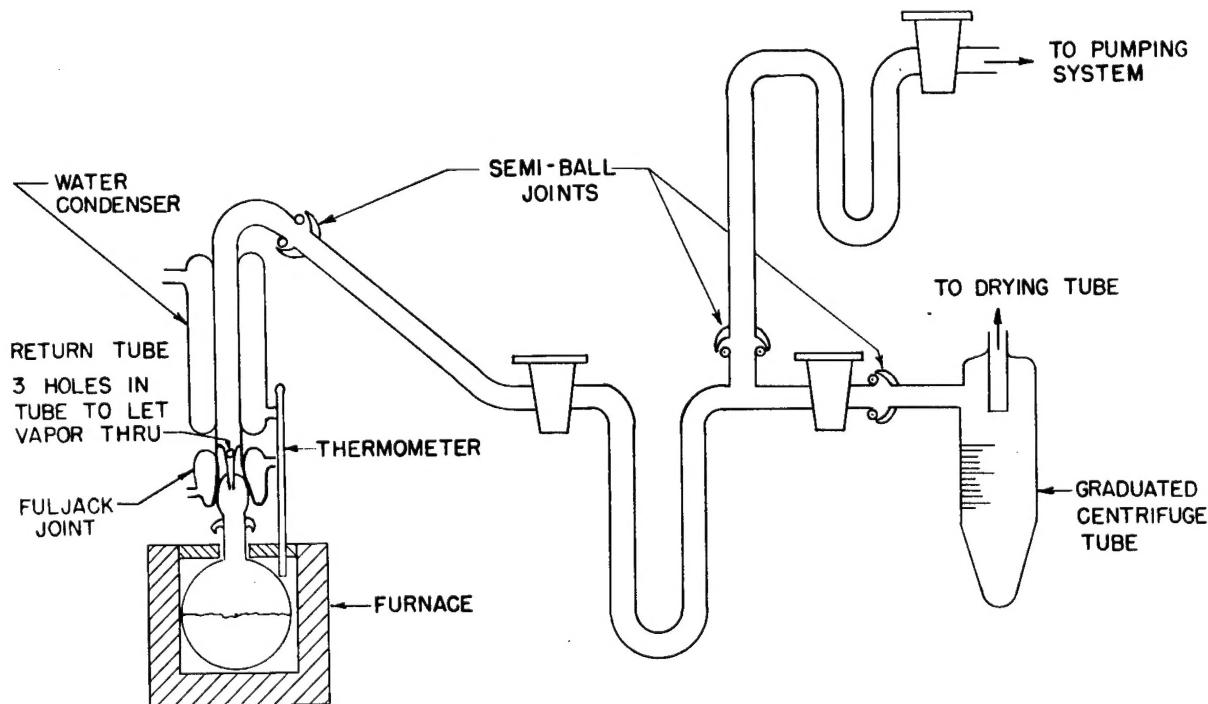


Figure 1.

Figure 2. Apparatus used for the conversion of  $\text{Me}_2\text{O}\cdot\text{BF}_3$  into calcium fluoborate.

The  $\text{CaF}_2 \cdot \text{BF}_3$  compound forms a hard cake in the reaction flask, and the same bulb is therefore used for the next step.

### Step 3

The thermal decomposition of the  $\text{CaF}_2 \cdot \text{BF}_3$  compound is done with the apparatus shown in Figure 3. It is believed desirable to outgas the solid before generating and collecting the  $\text{BF}_3$ . This is done to remove any residual  $\text{SiF}_4$  which might remain in the mixture as well as to minimize the amount of air which might be trapped in the subsequent collection of the  $\text{BF}_3$ . An arbitrary criterion is followed to determine when the solid has been sufficiently outgassed. The system is usually pumped on with the reaction bulb kept at  $100^\circ\text{C}$  until the pressure in the system becomes less than  $10^{-3}$  millimeters Hg as measured on the McLeod gauge. The amount of  $\text{BF}_3$  lost during this process is trivial since the decomposition pressure of the solid is quite small at  $100^\circ\text{C}$ .

The decomposition of the calcium fluoborate is done at about  $250^\circ\text{C}$ . A plug of glass wool is kept in the neck of the decomposition flask to prevent any  $\text{CaF}_2$  from blowing into the system. The first U-tube is kept at dry ice temperature, the  $\text{BF}_3$  being collected in the second U-tube at liquid air temperature. A brown liquid, probably resulting from the decomposition of  $\text{BF}_3$  due to the presence of water, is usually collected in the first U-tube. The system is pumped on at all times during the decomposition, since the solid has not been thoroughly degassed.

If the U-tube in which the  $\text{BF}_3$  is being collected becomes plugged with  $\text{BF}_3$ , the decomposition is stopped and the  $\text{BF}_3$  transferred to the storage bulb. Fluocarbon stopcock grease is used in the decomposition line, while Apiezon M or N is used in the storage and pumping line.

The overall yield of  $\text{BF}_3$  from Steps 2 and 3 is about 90%.

### STORAGE OF $\text{BF}_3$ AND FILLING OF CHAMBERS

Because of the danger of fractionation in the preparation of  $\text{BF}_3$  described, it is desirable to carry both of the steps to completion. This is particularly necessary if the gas is to be used as a relative standard representative of the total supply of starting material. Therefore, a suitable method of storage is necessary.

The gas has been successfully stored in a well outgassed glass bulb for many months at a time. Since  $\text{BF}_3$  reacts with all the stopcock greases which we have tried and is inert to mercury, a mercury valve is used. The valve is shown in Figure 4 and consists of a U-tube with ground glass check valves. Vacuum and air are used to lower and raise the mercury in the reservoir. The stainless steel valve is included to facilitate any transfer operations as well as to provide a guard against failure of the check valves.

Chambers are always thoroughly outgassed before filling. They are pumped down to a "stick" vacuum on the McLeod, which must persist even after heating them. For fillings above atmospheric pressure, the metal system is used. The stainless steel valves used are repacked with poly TFE before being used with  $\text{BF}_3$ . Chambers to be filled to atmospheric pressure or less are fitted with a glass semi-ball joint in order to attach them to the apparatus. Since  $\text{BF}_3$  does not react rapidly with stopcock grease, Apiezon grease is used on the stopcocks in the filling line.

Well-constructed chambers filled with the gas may by this method have been found to show constant operational characteristics over long periods of time. In most instances these chambers are connected to the filling line with 1/8 inch copper tubing. The tubing is then pinched off and sealed closed after filling.

The gas in the 3-liter storage bulb is then completely vaporized before taking an aliquot to fill a chamber. It is necessary to freeze the  $\text{BF}_3$  down into the cold finger in order to open the mercury valve. The system is usually pumped on at this point to remove any small amount of inert gas which may be present.

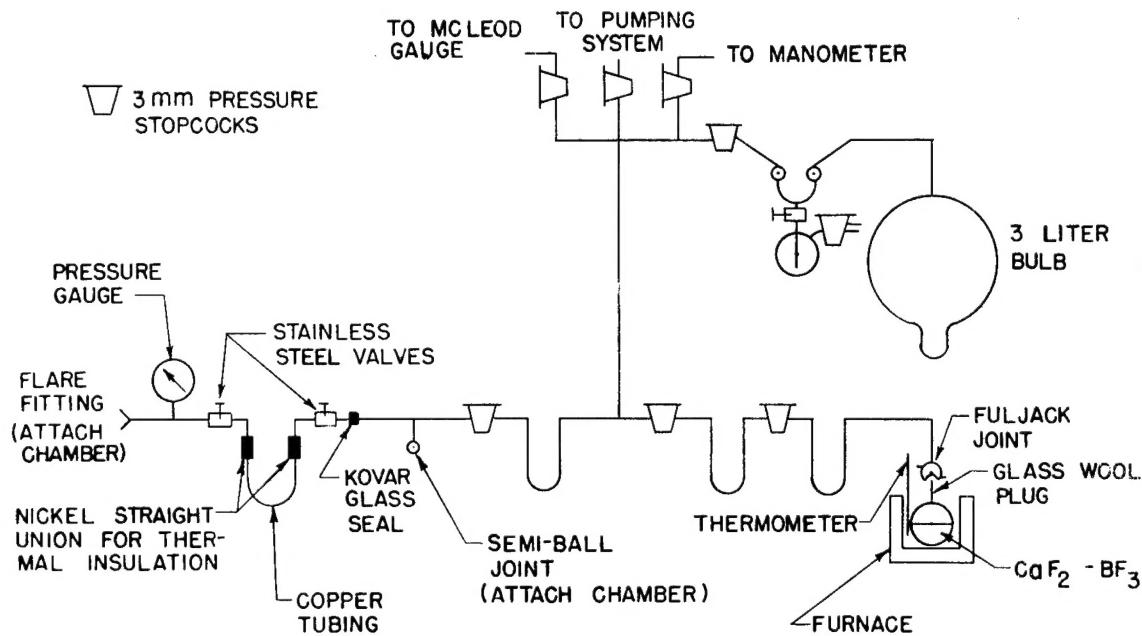


Figure 3. Apparatus used for the thermal decomposition of the  $\text{CaF}_2 \cdot \text{BF}_3$  compound.

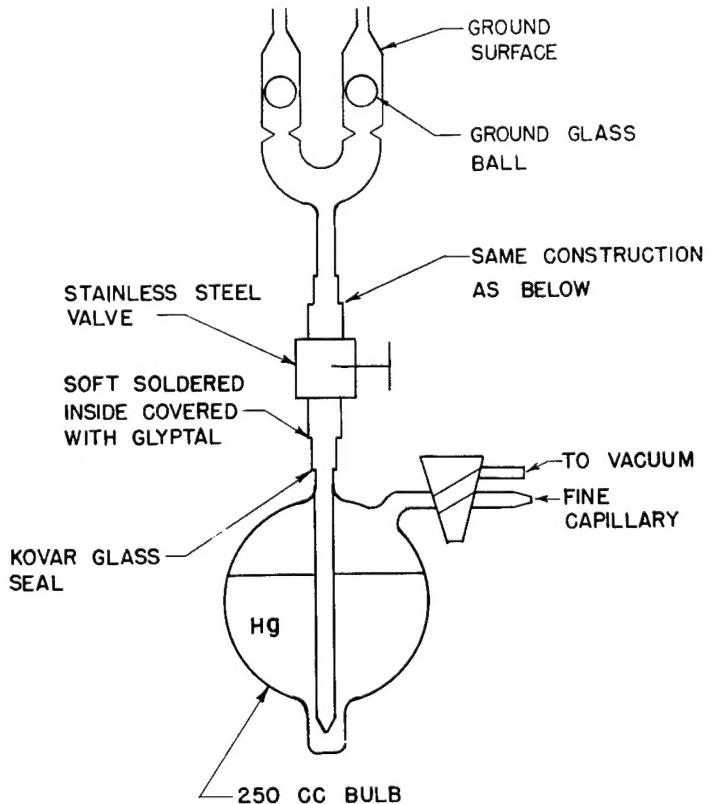


Figure 4. Mercury valve.

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